



Characterization of the transient species generated in the photoexcitation of benzoic acid, 2-hydroxy-, 2-D-ribofuranosylhydrazide

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ARTICLE INFO

Article history:

Received 18 May 2009

Received in revised form 10 August 2009

Accepted 3 September 2009

Available online 8 September 2009

Keywords:

2-Hydroxy-, 2-D-ribofuranosylhydrazide (BHR)

Laser flash photolysis

Mono-photonic ionization

Pulse radiolysis

Radical

ABSTRACT

Using time-resolved technique of laser flash photolysis (LFP), it has been demonstrated that benzoic acid, 2-hydroxy-, 2-D-ribofuranosylhydrazide (BHR) in aqueous solution can be ionized via a mono-photonic process under 266 nm laser, giving a hydrated electron, anion radical that formed by hydrated electron reacts with steady state of BHR, and neutral radical that formed from rapid deprotonation of the radical cation of BHR. The quantum yield of photo-ionization is determined to be 0.024 at room temperature. Furthermore studies on the reaction of BHR with the primary irradiated products of water such as e_{aq}^- and $^{\bullet}OH$, and with $^{\bullet}N_3$ have been determined. On the basis of comparison of the results from LFP with that obtained from time-resolved pulse radiolysis, the reaction mechanism has unambiguously identified.

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1. Introduction

Photodynamic therapy (PDT) has been applied in many aspects, such as the treatment of variety of tumors, the purification of blood products [1–3] and photo-induced inactivation of viruses [4]. PDT is based on that the photo-sensitizer can be concentrated in tumor cells and upon subsequent exposure to light in the presence of oxygen, specifically used to destroy the tumor cells [5–7]. The consensus of opinion is that most PDT sensitizer acts via the type II process involving energy transfer from triplet sensitizer to oxygen, producing cytotoxic singlet oxygen [8]. Alternative mechanisms exist that involve generation of radical species and are generally grouped under the type I reaction definition [9]. As part of the continuing research in this area, there has been a major search for better photo-sensitizer. This has resulted in part a large number of studies on modifying some existing photo-sensitizers through various synthetic methods.

Salicylic acid derivatives are widely used for the treatment of various diseases. For example, acetylsalicylic acid is the most widely used drug in the world, 4-aminosalicylic acid is used for tuberculosis treatment and diflunisal is a strong pain killer and antipyretic [10], and salicyhydroxamic acid and salicylic acid derivatives can be involved in proliferation inhibition of tumor

cells [11]. The wide ranging biological activities of salicylic acid derivatives in general and their anticancer activities in particular have generated considerable interest to study the physicochemical properties of them. Several studies show that in the aqueous solution under the 308 nm laser excitation, sulfosalicylic acid gives rise to the triplet state of the dianion, the hydrated electron and its radical anion [12,13]. Glycosides represent a group of molecules with immense biological applications and implications. It has been reported that the biological activity of butyrate can be tuned by sugars to improve its anticancer properties [14], as well as N-Glycosides of indole and of related compounds are of remarkable pharmacological relevance, e.g. as anticancer agents [15].

In our present paper, the photo-physical and photo-chemical behavior of a new kind of N-Glycoside salicylic acid derivative, benzoic acid, 2-hydroxy-, 2-D-ribofuranosylhydrazide (BHR, as shown in Scheme 1), was studied by means of laser flash photolysis (LFP) and pulse radiolysis. It has been demonstrated that exposure of BHR in aqueous solution to 266 nm laser light can give rise to mono-photonic ionization with high quantum yield. The transient species produced from LFP have been identified, and a series of related kinetic parameters have also been obtained.

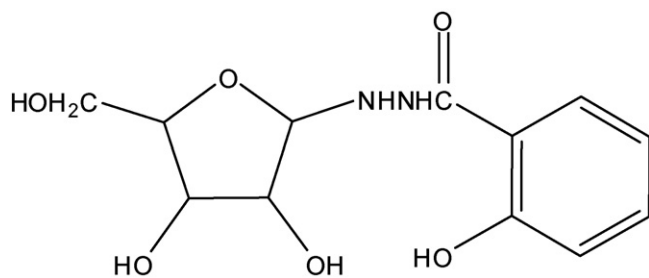
2. Experimental

2.1. Chemical reagents

BHR was kindly supplied by Dr SiChang Shao (Fuyang Normal College, Fuyang, China) and used without further purification. Its

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Scheme 1. Structure of BHR.

purity ($\geq 99\%$) was checked by HPLC. NaN_3 was purchased from Aldrich (Milwaukee, WI). $\text{K}_2\text{S}_2\text{O}_8$ (analytic grade) was recrystallized from triply distilled water. *Tert*-Butyl alcohol (*t*-BuOH) was distilled before use. NaOH, HClO_4 and phosphate (analytic grade reagent) were commercially available and used without further purification.

Unless otherwise indicated, all solutions were freshly prepared with triply distilled water, buffered with 2 mM phosphate (pH = 7) and protected from light at all times. The pH value of the solution was adjusted by adding NaOH, HClO_4 or phosphate solution. The solutions were deaerated with high-purity N_2 ($\geq 99.99\%$), N_2O , or O_2 ($\geq 99.5\%$) for different purposes by bubbling for at least for 20 min prior to the experiments. For the determination of the quantum yield of photo-ionization ($\Phi_{\text{e}_{\text{aq}}^-}^{\text{BHR}}$) in aqueous solution, an N_2 -saturated aqueous solution of potassium iodide (KI, analytic grade reagent, recrystallized from triply distilled water) with the same optical density (OD) at 266 nm was used as a reference (the quantum yield of e_{aq}^- , $\Phi_{\text{e}_{\text{aq}}^-} = 0.23$) [16]. Ground-state absorption properties were studied using a UV-vis spectrometer (VARIAN CARY 50 Probe). All experiments were performed in a 1 cm quartz cuvette at room temperature.

2.2. Laser flash photolysis experiments

Laser flash photolysis experiments were carried out using Nd: YAG laser of 266 nm light pulses with a duration of 5 ns and the maximum energy of 40 mJ per pulse used as the pump light source. A xenon lamp was employed as detecting light source. The laser and analyzing light beam passed perpendicularly through a quartz cell with an optical path length of 10 mm. The transmitted light entered a monochromator equipped with an R955 photomultiplier. The output signal from the Agilent 54830B digital oscillograph was transferred to a personal computer for data treatment. The LFP setup has been previously described [17–19].

2.3. Pulse radiolysis experiments

Pulse radiolysis experiments were conducted using a linear accelerator providing an 8 MeV electron pulse with a duration of 5 ns determined by a thiocyanate dosimeter containing 20 mM KSCN solution saturated with N_2O , and by taking $\epsilon_{(\text{SCN})_2}^- = 7600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 480 nm. The light source used for the analysis was a 300 W xenon lamp. The electron beam and the light beam passed perpendicularly through a quartz cell with an optical length of 10 mm. The transmitted light entered a monochromator equipped with a photomultiplier (Hamamatsu R955). Detailed descriptions of the set up of the pulse radiolysis equipment and experimental conditions have been given elsewhere [20].

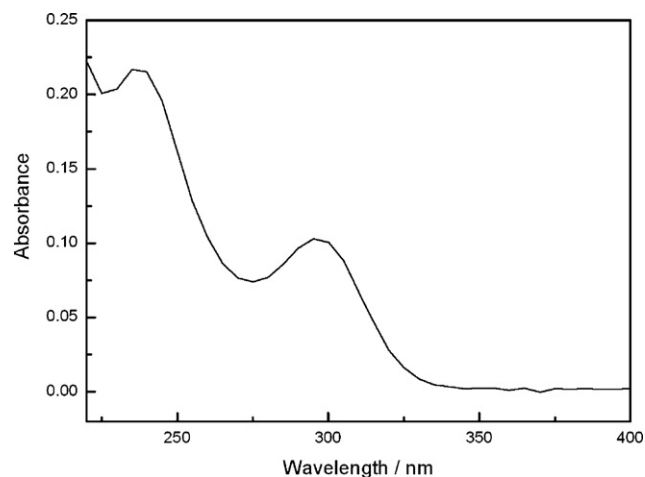


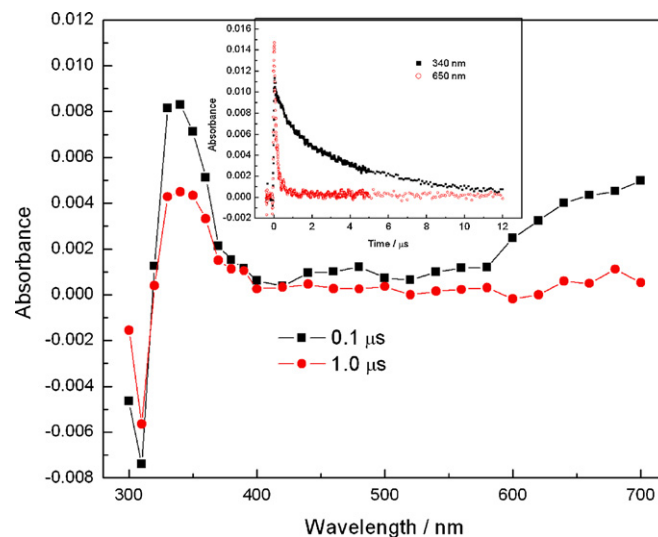
Fig. 1. Absorption spectrum of BHR dissolved in aqueous solution at pH = 7 (0.5 mM).

3. Results and discussion

3.1. Characterization of photo-ionization of BHR in aqueous solution

3.1.1. Monophonic ionization of BHR

The UV-vis spectrum of BHR in aqueous solution shows a strong absorption peak at 220, 235 and 295 nm respectively, as shown in Fig. 1. The absorbance of 0.1 at 266 nm with 0.5 mM BHR is suitable for 266 nm LFP. As shown in Fig. 2, the transient absorption spectra from 266 nm LFP of a 0.5 mM deaerated solution of BHR at about 0.1 μs after laser pulse are characterized by two main features. These include a strong and broad absorption band from 500 to 700 nm and a strong absorption band with $\lambda_{\text{max}} = 340 \text{ nm}$ as shown in inset of Fig. 2. The transient species with absorption band from 500 to 700 nm decay fast, and the absorption-time profile observed at 650 nm can be efficiently removed by N_2O -saturated with addition of *t*-BuOH in the solution (Eqs. (2) and (3)) (Fig. 3), thus it should be assigned to the hydrated electron (e_{aq}^-) [21]. This means that BHR is photo-ionized by 266 nm light to produce e_{aq}^- (Eq. (1)) [22], which can be scavenged by N_2O to produce OH^- and $\cdot\text{OH}$ as shown

Fig. 2. Transient absorption spectra obtained from 266 nm LFP of N_2 -saturated 0.5 mM BHR aqueous solution at pH = 7 recorded at: (■) 0.1 μs , (●) 1 μs after laser pulse. Inset: transient absorption curve observed at 340 nm (■), 650 nm (○), respectively.

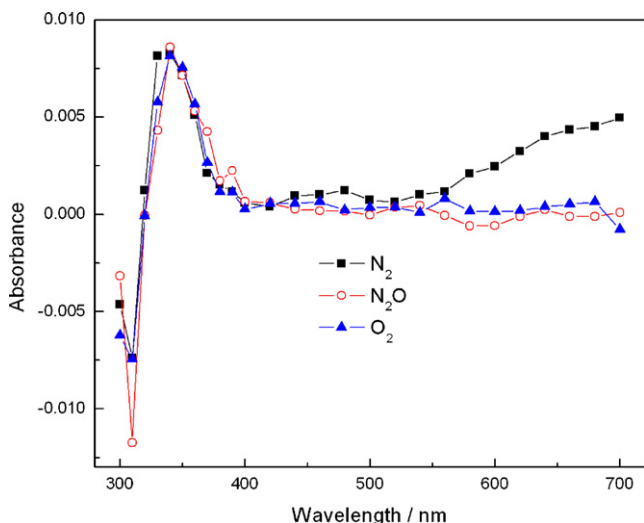
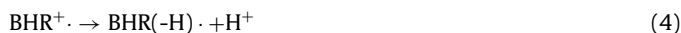
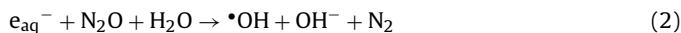


Fig. 3. Transient absorption spectra obtained from 266 nm LFP of N_2 -saturated (■), N_2O -saturated (○) with 0.1 M *t*-BuOH added, or O_2 -saturated (▲) 0.5 mM BHR aqueous solution at pH = 7 recorded at 0.1 μ s after laser pulse, respectively.

in Eq. (2) and can be captured by O_2 to produce $O_2^{\bullet-}$. And $\bullet OH$ can be further scavenged by additive of *t*-BuOH as shown in Eq. (3) and there is no any transient absorption in detecting region of 300–700 nm with $O_2^{\bullet-}$. The transient species with the maximum absorption at 340 nm, which cannot be quenched in N_2O or O_2 -saturated system, as shown in Fig. 3, can be mainly assigned to the contribution of $BHR^{\bullet+}$ or deprotonated transient product ($BHR(-H)^{\bullet}$) (Eq. (4)). The further identification of it will be mentioned in this paper later:



In order to determine whether the photo-ionization of BHR by 266 nm photons is caused by a monophoton or a biphoton process, the yield of e_{aq}^- (at 650 nm which the ratio of signal/noise is higher) measured from the OD value at 0.1 μ s after laser pulse was found to increase linearly with the incident laser intensity (I_L) as shown in Fig. 4. The ionization therefore proceeds via a mono-photonic pro-

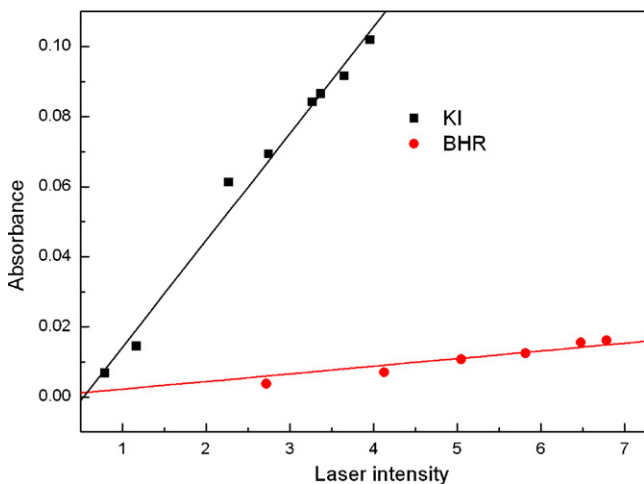


Fig. 4. Dependence on laser intensity of the absorbance at 650 nm immediately after the 266 nm laser pulse: (■) KI and (●) BHR.

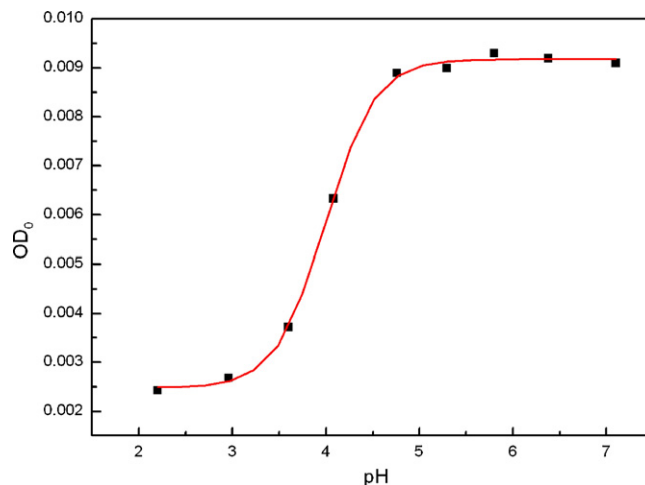


Fig. 5. Absorbance at 340 nm as a function of pH dependence, recorded immediately after the 266 nm laser pulse.

cess under our experimental conditions. From the slope at 650 nm, the quantum yield of the photo-ionization (Φ_{BHR}) is determined to be 0.024 relative to that for potassium iodide.

3.2. Identification and the characters of $BHR^{\bullet+}$

The transient absorption of $BHR^{\bullet+}$ observed at 340 nm was investigated by changing pH value of the N_2O -saturated with 0.1 M *t*-BuOH added 0.5 mM BHR aqueous solution as shown in Fig. 5. And pK_a value of $BHR^{\bullet+}$ is determined to be 4.0 [23]. This means that at pH = 7 $BHR^{\bullet+}$ is changed into $BHR(-H)^{\bullet}$ via deprotonation (Eq. (4)). The long-lived transient species produced in 266 nm LFP with maximum absorption at 340 nm shown in Fig. 2 must be assigned to $BHR(-H)^{\bullet}$. However, the laser photolysis of BHR cannot be made in acidic aqueous solution (pH < 2) as the molecular structure of BHR may be changed. So all of the kinetic study on BHR should be performed at pH > 2.

Since the $BHR^{\bullet+}$ and e_{aq}^- are formed in stoichiometric amounts, the molar extinction coefficient of $BHR^{\bullet+}$ ($\epsilon_{BHR^{\bullet+}}$) was determined using e_{aq}^- as an internal standard [24]. By comparing the transient absorbance OD_0 after laser pulse at 650 and 340 nm respectively, the $\epsilon_{BHR^{\bullet+}}$ can be deduced via the following equation [25]:

$$OD_{0\lambda} = \epsilon_{\lambda} C_{\lambda} L \quad (5)$$

$$OD_{0\lambda} = \epsilon_{\lambda} C_{\lambda} L \quad (6)$$

$$(5)/(6) \quad \epsilon_{\lambda} OD_{0\lambda} = \epsilon_{\lambda} OD_{0\lambda} \quad (7)$$

where $\epsilon_{\lambda=650\text{nm}}$ and $OD_{0\lambda=650\text{nm}}$ are the molar extinction coefficient and the OD_0 value of e_{aq}^- recorded at the wavelength of 650 nm in N_2 -saturated aqueous solution, respectively. $\epsilon_{\lambda=340\text{nm}}$ and $OD_{0\lambda=340\text{nm}}$ are the molar extinction coefficient and the OD_0 value of $BHR^{\bullet+}$ recorded at the wavelength of 340 nm in O_2 -saturated aqueous solution to suppress the effect of e_{aq}^- . $\epsilon_{\lambda=650\text{nm}}$ has been reported to be $14,900 \text{ M}^{-1} \text{ cm}^{-1}$ [21], hence $\epsilon_{BHR^{\bullet+}}$ can be calculated as $8880 \text{ M}^{-1} \text{ cm}^{-1}$. However, as the $BHR^{\bullet+}$ should be transferred into $BHR(-H)^{\bullet}$ at pH = 7, here the value of $8880 \text{ M}^{-1} \text{ cm}^{-1}$ should exactly be the molecular extinguish of $BHR(-H)^{\bullet}$ and $\epsilon_{BHR^{\bullet+}}$ of $BHR^{\bullet+}$ should be smaller than that of $8880 \text{ M}^{-1} \text{ cm}^{-1}$ at 340 nm though at pH below 4 (see Fig. 5).

3.3. Generation of oxidized BHR radical by the use of $SO_4^{\bullet-}$

To further identify $BHR^{\bullet+}$, reaction of BHR with sulfate radical ($SO_4^{\bullet-}$) was investigated. As a one-electron oxidant, $SO_4^{\bullet-}$ can be generated easily with 266 nm LFP from $S_2O_8^{2-}$ (Eq. (8)).

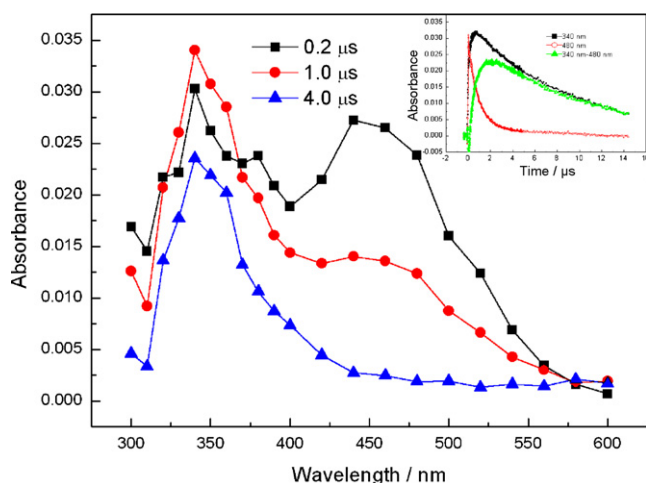
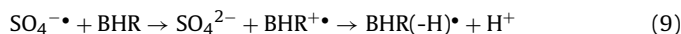


Fig. 6. Transient absorption spectra recorded at (■) 0.2 μs, (●) 1.0 μs and (▲) 4.0 μs after 266 nm LFP of deaerated solutions at pH=7 containing 0.1 M $K_2S_2O_8$ and 0.1 mM BHR. Inset: transient time profile observed at 340 nm (■), 480 nm (○), and set up and decay curve of $BHR(-H)^*$ (▲) obtained by subtracting 480 nm from 340 nm, respectively.

Photolysis of 0.1 M $K_2S_2O_8$ neutral aqueous solution showed the formation of $SO_4^{\cdot-}$ with maximum absorption spectra at 350 and 460 nm (data not shown) [26–28]. Concentrations of $S_2O_8^{2-}$ and BHR must be carefully designed to make sure that $S_2O_8^{2-}$ is principal absorber of 266 nm light and the photolysis of BHR can be ignored. Then the transient absorption spectra of reaction (9) can be recorded. The transient absorption spectra recorded at 0.2, 1.0 and 4.0 μs after 266 nm LFP of N_2 -saturated neutral aqueous solution containing 0.1 M $K_2S_2O_8$ and 0.1 mM BHR are shown in Fig. 6. An increment of absorbance at 340 nm was observed, which indicated that new transient species was formed. As shown in inset of Fig. 6, the growth trace of $BHR(-H)^*$ at 340 nm was obtained by subtracting the absorbance of $SO_4^{\cdot-}$ at 480 nm (The values have a little difference to the normal value, which is due to the absorbent interaction between $BHR(-H)^*$ and $SO_4^{\cdot-}$). The transient species with absorption peak at 340 nm could be assigned as $BHR(-H)^*$ formed according to the following mechanism:



From a plot of the observed pseudo-first-order decay rate constant K_{obs} at 480 nm versus the BHR concentration at pH=7, the rate constant for the formation of the oxidized $BHR^{\cdot+}$ can be determined to be $2 \times 10^9 M^{-1} s^{-1}$ [29].

3.4. Pulse radiolysis of BHR in a flow system

The radiolysis of dilute aqueous solution saturated with N_2 leads to the production of three primary highly reactive intermediates (e_{aq}^- , $\cdot OH$, $\cdot H$) as shown in reaction (10), with $G(\cdot OH) = G(e_{aq}^-) = 2.8$ and $G(\cdot H) = 0.6$, besides other less reactive molecular compounds (H_{aq}^+ , H_2 , H_2O_2) [30]. The possibility of the reaction of them with BHR may occur:



3.5. Reaction of BHR with e_{aq}^-

The transient absorption spectra with a strong broad band characterized by the peak at 700 nm (as shown in Fig. 7) can be observed immediately after pulse radiolysis of N_2 -saturated aqueous solution containing 0.2 mM BHR and 0.3 M *t*-BuOH with 2 mM

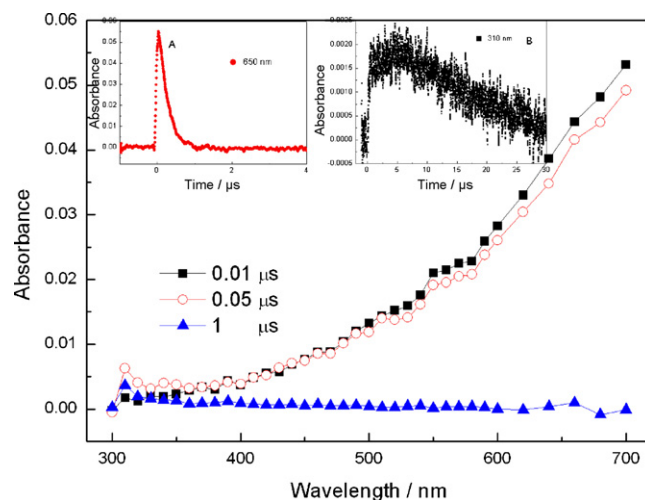


Fig. 7. Transient absorption spectra from pulse radiolysis of N_2 -saturated aqueous solution containing 0.2 mM BHR and 0.3 M *t*-BuOH at pH=7 recorded at: (■) 0.01 μs, (○) 0.05 μs, (▲) 1 μs. Inset: (A) The absorption–time profile at 650 nm. (B) The absorption–time profile at 310 nm.

phosphate buffer at pH=7. Obviously it is the characteristic absorption of the hydrated electron (e_{aq}^-). Furthermore, a new transient species with maximum absorption at 310 nm for BHR forms up accompanying with the decay of e_{aq}^- . As shown in the insets (A) and (B) of Fig. 7, the formation process observed at 310 nm is synchronous with the decay of e_{aq}^- recorded at 650 nm. When the solution was saturated with N_2O , all of them disappeared. Thus the new absorption was attributed to be one-electron reduction specie, the radical anion of BHR ($BHR^{\cdot-}$) [31]. From the observed decay kinetics of e_{aq}^- recorded at 650 nm which depends linearly on BHR concentrations in deaerated solution, the first-order reaction rate constant of $BHR^{\cdot-}$ induced by e_{aq}^- has been obtained as $1 \times 10^{10} M^{-1} s^{-1}$ at pH=7. So it can be concluded that BHR can be reduced by e_{aq}^- to produce $BHR^{\cdot-}$ (Eq. (11)). However in the LFP of BHR, the absorption of $BHR^{\cdot-}$ was not observed, the potential reason of which could be its molar extinction coefficient far less than $BHR^{\cdot+}$ and its transient absorption is interrupted by $BHR^{\cdot+}$:



3.6. Reaction with $\cdot OH$ radical

The transient absorption spectra with $\lambda_{max} = 330$ nm obtained in pulse radiolysis of N_2O -saturated aqueous solution containing 0.15 mM BHR buffered with 2 mM phosphate are displayed in Fig. 8. The transient absorption band will disappear in the presence of *t*-BuOH as an efficient $\cdot OH$ scavenger. With combination of the absorption–time profile of 330 nm as shown in inset (B) of Fig. 8, it could be derived that the transient absorption with maximum absorption at 330 nm is from contribution of reaction of $\cdot OH$ with BHR (Eq. (12)) [32], in which there may be three kinds of reaction mechanism involved. At first, $\cdot OH$ can attack the phenoxy anion to produce phenoxy radical of BHR via one electron transfer. The secondly, $\cdot OH$ can adduct on the phenyl ring to produce (OH-BHR) \cdot and $\cdot OH$ can also abstract hydrogen from BHR to produce neutral radical of BHR. So the transient species formed in the reaction may come from three different processes and the forming process of the transient species is complex:



From kinetic analysis of the growth trace of this radical product, the observed pseudo-first-order rate constant was obtained in the experiment. By varying the concentration of BHR, a series of

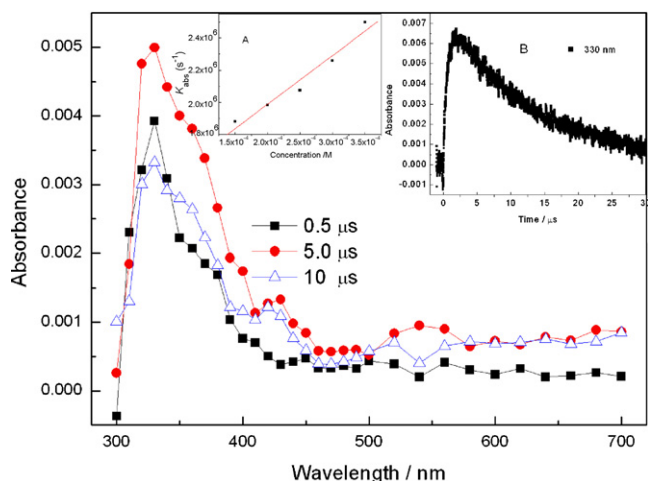


Fig. 8. Transient absorption spectra obtained in pulse radiolysis of N_2O -saturated aqueous solution containing 0.15 mM BHR at pH = 7 recorded at: (■) 0.5 μs , (●) 5.0 μs , (▲) 10 μs . Inset: (A) The observed BHR(-H) * set up first-order rate constant (K_{obs}) recorded at 330 nm against BHR ground state concentration. (B) The absorption–time profile at 330 nm.

observed constants were obtained as shown in inset (A) of Fig. 8, and the rate constant for reaction of *OH with BHR was derived to be $3 \times 10^9 M^{-1} s^{-1}$.

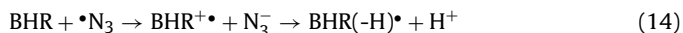
3.7. One-electron oxidation of BHR by the use of *N_3

*N_3 is proved to be a milder one-electron oxidant in many studies of antioxidants [33–35]. It has a very narrow absorption band at ~ 274 nm and little absorption above 300 nm [33,36] which provide an important advantage for study of radical cation in pulse radiolysis studies since it readily allows measurements on many transients in a special region where radicals such as $Br_2^{\bullet-}$, $SO_4^{\bullet-}$ and $(SCN)_2^{\bullet-}$ mask observations in short time [37–39]. As a result, it can be used to directly examine the production of the oxidized products and study details of the oxidation process even when the initial radical is present. Thus, to further identify and investigate the BHR * , *N_3 was used as one-electron oxidant model in this study. As secondary oxidant, it was formed by pulse radiolysis of 20 mM NaN_3 aqueous solution saturated with N_2O . Under such conditions, the primary radical *OH totally formed from irradiation of aqueous solution was converted into *N_3 radical as shown in Eq. (13):



With the concentration of 20 mM azide and 0.15 mM BHR, 99% of *OH radical was converted to *N_3 radical on the nanosecond time scale, which ensured *OH radical would not interfere with the secondary kinetics.

Upon pulse radiolysis of NaN_3 solution saturated with N_2O at pH = 7 and containing BHR, the transient absorption spectra with maximum absorption peak at 340 nm was obtained as shown in Fig. 9, which is very similar to that from photolysis of BHR in N_2O and O_2 -saturated neutral aqueous solution (Fig. 3), thus the absorption peak at 340 nm should be assigned to BHR(-H) * produced from deprotonation of BHR * , the formation mechanism of which could be shown as Eq. (14):



Considering the best signal to noise ratio, the absorption–time profile at 360 nm was shown in the inset (B) of Fig. 9. From kinetic analysis of the growth process of BHR(-H) * at 360 nm (as shown in inset (A) of Fig. 9), the reaction rate constant for oxidation of BHR by *N_3 was calculated to be $5 \times 10^9 M^{-1} s^{-1}$.

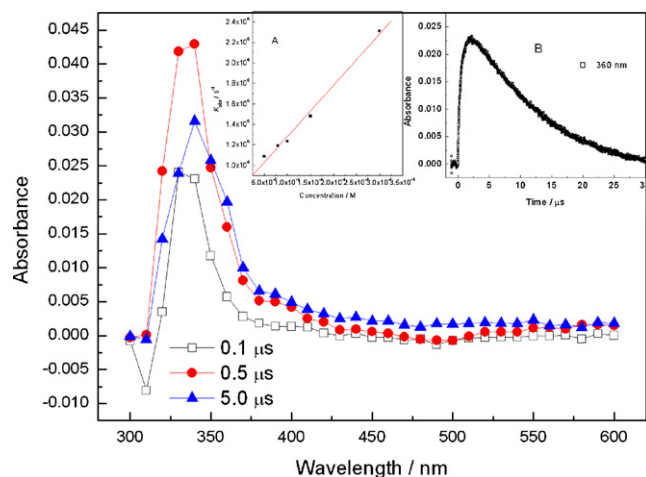


Fig. 9. Transient absorption spectra from pulse radiolysis of N_2O -saturated aqueous solution containing 0.15 mM BHR and 20 mM NaN_3 at pH = 7 recorded at: (□) 0.1 μs , (●) 0.5 μs , (▲) 5.0 μs . Inset: (A) The observed BHR(-H) * set up first-order rate constant (K_{obs}) recorded at 360 nm against BHR ground state concentration. (B) The absorption–time profile at 360 nm.

4. Conclusion

As a synthetic N-Glycoside salicylic acid derivative drug, the photo-chemical and photo-physical properties of BHR has been studied by LFP and pulse radiolysis. It has been demonstrated that photo-ejection of an electron from BHR via a mono-photonic process on exposure to 266 nm light leads to the generation of BHR $^{\bullet-}$ and BHR * . The quantum yield of photo-ionization was determined to be 0.024 at room temperature. The radical cation of BHR converts into the neutral radical via fast deprotonation in neutral aqueous solution. Furthermore, time-resolved pulse radiolysis has been used to confirm the reaction of BHR with e_{aq}^- , *OH and *N_3 with the rate constants of 1×10^{10} , 3×10^9 , and $5 \times 10^9 M^{-1} s^{-1}$, respectively. From these results, we can further deduce that BHR can be easily oxidized to produce its radical species, which may attack biological tissue and macromolecules via electron transfer subsequently meanwhile BHR may be used in PDT as a potential photo-sensitizer. A series studies involved in the reaction of BHR radicals with biological system are carried out in our group and the results will be reported in another paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 50673078), the 863 Project of the Ministry of Science and Technology (No. 2007AA022004) and the Project of Shanghai (No. 08ZZ21).

References

- [1] J.L. Matthews, J.T. Newman, F. Sogandares-Bernal, M.M. Judy, H. Skiles, J.E. Leveson, A.J. Marergo-Rowe, T.C. Chanh, Photodynamic therapy of viral contaminants with potential for blood banking applications, *Transfusion* 28 (1988) 81–83.
- [2] H. Margolis-Nunno, E. Ben-Hur, P. Gottlieb, R. Robinson, J. Oetjen, B. Horowitz, Inactivation by phthalocyanine photosensitization of multiple forms of human immunodeficiency virus in red cell concentrates, *Transfusion* 36 (1996) 743–750.
- [3] A.C. Moor, A. Van der Veen, A.E. Wagenaars van Gompel, T.M. Dubbelman, J. Van Stevenink, A. Brand, Shelf-life of photodynamically sterilized red cell concentrates with various numbers of white cells, *Transfusion* 37 (1997) 592–600.
- [4] F. Sieber, J.M. O'Brien, D.K. Gajney, Merocyanine-sensitized photoinactivation of enveloped viruses, *Blood Cells* 18 (1992) 117–128.
- [5] M. Ochser, Photophysical and photobiological processes in the photodynamic therapy of tumors, *J. Photochem. Photobiol. B* 39 (1997) 1–18.

- [6] R. Bonnett, Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy, *Chem. Soc. Rev.* 24 (1995) 19–33.
- [7] I.J. Macdonald, T.J. Dougherty, Basic principles of photodynamic therapy, *J. Porphyr. Phthalocya.* 5 (2001) 105–129.
- [8] T.C. Oldham, D. Phillips, A.J. MacRobert, Attempts to measure sensitizer photo-physic in opaque tissue, *J. Photochem. Photobiol. B* 61 (2001) 129–136.
- [9] C.S. Foote, Definition of type I and type II photosensitized oxidation, *Photochem. Photobiol.* 54 (1991) 659.
- [10] E. Bayram, M. Senturk, O.I. Kufrevioglu, C.T. Supuran, In vitro inhibition of salicylic acid derivatives on human cytosolic carbonic anhydrase isozymes I and II, *Bioorg. Med. Chem.* 16 (2008) 9101–9105.
- [11] U. Salzmann, P. Ludwig, T. Schewe, S.M. Rapoport, The share of lipoxygenase in the antimycin-resistant oxygen uptake of intact rabbit reticulocytes, *Biomed. Biochim. Acta* 44 (2) (1985) 213–221.
- [12] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, A.I. Kruppa, H. Lemmetyinen, Photochemistry of sulfosalicylic acid in aqueous solutions, *J. Photochem. Photobiol. A* 162 (2004) 153–162.
- [13] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, N.M. Bazhin, E. Vauthier, Photolysis of sulfosalicylic acid in aqueous solutions over a wide pH range, *J. Photochem. Photobiol. A* 181 (2006) 37–43.
- [14] S.G. Sampathkumar, M.B. Jones, M.A. Meledeo, C.T. Campbell, S.S. Choi, K. Hida, P. Gomutputra, A. Sheh, T. Gilmartin, S.R. Head, K.J. Yarema, Targeting glycosylation pathways and the cell cycle: sugar-dependent activity of butyrate–carbohydrate cancer prodrugs, *Chem. Biol.* 13 (2006) 1265–1275.
- [15] K.M. Driller, S. Libnow, M. Hein, M. Harms, K. Wende, M. Lalk, D. Michalik, H. Reinke, P. Langer, Synthesis of 6H-indolo[2,3-b]quinoxaline-N-glycosides and their cytotoxic activity against human ceratinocytes (HaCaT), *Org. Biomol. Chem.* 6 (2008) 4218–4223.
- [16] J. Jortner, M. Ottolenghi, G. Stein, On the photochemistry of aqueous solutions of chloride, bromide, and iodide ions, *J. Phys. Chem.* 68 (1964) 247–255.
- [17] L.L. Cheng, M. Wang, P. Zhao, H. Zhu, R.R. Zhu, X.Y. Sun, S.D. Yao, S.L. Wang, The examination of berberine excited state by laser flash photolysis, *Spectrochim. Acta Part A* 73 (2009) 268–272.
- [18] P. Zhao, M. Wang, S.P. Zhang, S.C. Shao, X.Y. Sun, S.D. Yao, S.L. Wang, Photochemical properties of a new kind of anti-cancer drug: N-glycoside compound, *Sci. China Ser. B: Chem.* 51 (2008) 872–877.
- [19] L.L. Cheng, P. Zhao, M. Wang, H. Zhu, R.R. Zhu, X.Y. Sun, S.L. Wang, Photodamage and photooxidation mechanisms of bovine serum albumin, *Acta Phys. –Chim. Sin.* 25 (2009) 25–29.
- [20] D.Y. Dou, Y.B. Liu, H.W. Zhao, L. Kong, S.D. Yao, Radiolysis and photolysis studies on active transient species of diethylstilbestrol, *J. Photochem. Photobiol. A* 171 (2005) 209–214.
- [21] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O⁻) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [22] C.Y. Lu, W.F. Wang, W.Z. Lin, Z.H. Han, J.X. Pan, S.D. Yao, N.Y. Lin, Monophotonic ionization of etoposide in aqueous solution by 248 nm laser light: identification of transient intermediates, *J. Photochem. Photobiol. B* 49 (1999) 61–64.
- [23] H.Y. Fu, Y. Katsumura, M.Z. Lin, Y. Muroya, Laser photolysis and pulse radiolysis studies on silybin in ethanol solutions, *Radiat. Phys. Chem.* 77 (2008) 1300–1305.
- [24] G. Trampe, J. Mattay, S. Steenken, Ionization of 1,3-dioxoles in aqueous solution by 248-nm laser flash photolysis: characterization of the radical cations, *J. Phys. Chem.* 93 (1989) 7157–7160.
- [25] H.J. Ma, M. Wang, C.Y. Pu, J. Zhang, S.F. Zhao, S.D. Yao, J. Xiong, Transient and steady-state photolysis of p-nitroaniline in aqueous solution, *J. Hazard. Mater.* 165 (2009) 867–873.
- [26] H.P. Zhu, Z.X. Zhang, H.W. Zhao, W.F. Wang, S.D. Yao, Transient species and its properties of melatonin, *Sci. Chin. B: Chem.* 49 (2006) 308–314.
- [27] K.L. Ivanov, E.M. Glebov, V.F. Plyusnin, Y.V. Ivanov, V.P. Grivin, N.M. Bazhin, Laser flash photolysis of sodium persulfate in aqueous solution with additions of dimethylformamide, *J. Photochem. Photobiol. A* 133 (2000) 99–104.
- [28] Y. Tang, R.P. Thorn, R.L. Mauldin III, P.H. Wine, Kinetics and spectroscopy of the SO₄⁻ radical in aqueous solution, *J. Photochem. Photobiol. A: Chem.* 44 (1988) 243–258.
- [29] C.Y. Lu, W.F. Wang, W.Z. Lin, Z.H. Han, S.D. Yao, N.Y. Lin, Generation and photosensitization properties of the oxidized radical of riboflavin: a laser flash photolysis study, *J. Photochem. Photobiol. B* 52 (1999) 111–116.
- [30] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [31] C.Y. Lu, S.D. Yao, W.Z. Lin, W.F. Wang, N.Y. Lin, Y.P. Tong, T.W. Rong, Studies on the fullerol of C60 in aqueous solution with laser photolysis and pulse radiolysis, *Radiat. Phys. Chem.* 53 (1998) 137–143.
- [32] J.L. Miao, W.F. Wang, T.Y. Wu, D.Y. Dou, H.W. Zhao, S.D. Yao, R.L. Zheng, Studies on the reactions of sylvatesmin and lant beside with oxidizing free radicals, *Radiat. Phys. Chem.* 69 (2004) 25–29.
- [33] K.L. Priyadarsini, S.N. Guha, M.N.A. Rao, Physico-chemical properties and antioxidant activities of methoxy phenols, *Free Radic. Biol. Med.* 24 (1998) 933–941.
- [34] Z.B. Alfassi, R.H. Schuler, Reaction of azide radicals with aromatic compounds. Azide as a selective oxidant, *J. Phys. Chem.* 89 (1985) 3359–3363.
- [35] Y.C. Zhou, R.L. Zheng, Phenolic compounds and an analogue as superoxide anion scavengers and antioxidants, *Biochem. Pharm.* 42 (1991) 1177–1179.
- [36] E. Hayon, M. Simic, Absorption spectra and kinetics of the intermediate produced from the decay of azide radicals, *J. Am. Chem. Soc.* 92 (1970) 7486–7487.
- [37] D.E. Cabelli, B.H.J. Bielski, P.A. Seib, A pulse radiolysis study of the oxidation of methyl substituted ascorbates, *Radiat. Phys. Chem.* 23 (1984) 419–429.
- [38] P. Neta, V. Madhavan, H. Zemel, R.W. Fessenden, Rate constants and mechanism of reaction of SO₄^{-•} with aromatic compounds, *J. Am. Chem. Soc.* 99 (1977) 163–164.
- [39] S.V. Jovanovic, S. Steeken, Substituent effects on the spectral, acid–base and redox properties of indolyl radicals: a pulse radiolysis study, *J. Phys. Chem.* 96 (1992) 6674–6679.